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JAPANESE PATENT NO. HEI 7[1995]-278418
CALENDERABLE POLYESTER ELASTOMER COMPOSITION

Translated from Japanese into English
by Phoenix Translations Code No. 51-4373

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(19) JAPANESE PATENT OFFICE
(12) PATENT JOURNAL (A)
(11) KOKAI PATENT NO. HEI 7[1995]-278418

(51) Int. Cl.⁶: C08L 67/02
C08J 5/18
C08K 5/18
// B29C 43/24
(C08L 67/02
C08L 23:00
C08L 27:12
C08L 83:04)
B29K 67:00
B29L 7:00

Sequence No. for Office Use: 7365-4F

(21) Application No.: HEI 6[1994]-70651

(22) Application Date: April 8, 1994

(43) Publication Date: October 24, 1995

No. of Inventions: 8 (Total of 9 pages; OL)

Examination Request: Not requested

(54) Title: CALENDERABLE POLYESTER ELASTOMER COMPOSITION

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[There are no amendments to this patent application.]

(57) Abstract

Purpose

To provide polyester elastomer compositions having good calenderability and forming sheets and films with an excellent surface appearance and mechanical properties.

Constitution

Calenderable polyester elastomer compositions obtained by the melt blending of a polyester block copolymer mainly consisting of a: (A) high-melting crystalline polymer segment consisting of mainly a crystalline aromatic polyester unit and (B) a low-melting polymer segment consisting of mainly an aliphatic polyether unit and/or an aliphatic polyester unit, with at least one compound selected from a polyolefin wax, fluororesin powder, aromatic amine compound, and silicone resin powder.

Claims

1. Calenderable polyester elastomer composition obtained by the melt blending of 100 parts by weight of a polyester block copolymer mainly consisting of (A) high-melting crystalline polymer segment consisting of mainly a crystalline aromatic polyester unit and (B) a low-melting polymer segment consisting of mainly an aliphatic polyether unit and/or an aliphatic polyester unit, with 0.001-10 parts by weight of at least one compound selected from a polyolefin wax, fluororesin powder, aromatic amine compound, and silicone resin powder.
2. The calenderable polyester elastomer composition described in Claim 1, wherein the polyolefin wax has a number-average molecular weight below 50,000.
3. The calenderable polyester elastomer composition described in Claim 2, wherein the polyolefin wax is a modified polyolefin wax.
4. The calenderable polyester elastomer composition described in Claim 3, wherein the polyolefin wax is a modified polyolefin wax having an acid value above 10 as measured according to JIS K5902.
5. The calenderable polyester elastomer composition described in any of Claims 1-4, wherein the polyolefin wax is a modified polyethylene wax.
6. The calenderable polyester elastomer composition described in Claim 1, wherein the fluororesin powder has average particle diameter below 100 µm.
7. The calenderable polyester elastomer composition described in Claim 1, wherein the aromatic amine compound is an aromatic secondary or tertiary amine compound.
8. The calenderable polyester elastomer composition described in Claim 1, wherein the silicone resin powder has an average particle diameter below 100 µm.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns polyester elastomer compositions having good calenderability, and forming sheets and films with an excellent surface appearance and mechanical properties.

[0002]

Conventional technology

Polyester block copolymers consisting of a crystalline aromatic polyester unit as the hard segment and an aliphatic polyether unit such as poly(alkylene oxide) glycol or an aliphatic polyester unit such as polylactone as the soft segment have excellent mechanical properties such as impact resistance, elastic recovery, softness, etc., as well as high-temperature properties, adhesive properties, etc., and their application range is wide, including industrial material such as sheets, films, fibers, etc., automobiles, electric and electronic parts, and various plastic molding methods can be used for fabrication. However, the calender molding process widely used for vinyl chloride, ethylene-vinyl acetate copolymer (EVA), and rubbers is rather limited for sheet and film formation.

[0003]

In the calender molding process, the resin is plasticized, defoamed, and kneaded in the groove between calender rolls at a high temperature and is drawn through the roll gap to the desired thickness. Polyester elastomers widely used for hot melt adhesives have a high tackiness thus have problems of excessive sticking and adhesion to rolls in calendaring. When the roll temperature is raised for easier plasticization and defoaming, the tackiness tends to increase further. On the other hand, the tackiness can be lowered by lowering the roll temperature, but since polyester elastomers are crystalline resins with definite melting points, when the roll temperature is lowered below the optimum temperature near the melting point, the plasticity is rapidly lost, making the formation of films in a stable manner very difficult. Currently, the calender molding process is essentially not possible for polyester elastomers.

[0004]

The technology for improving the calender processability of polyester elastomers is for the most part limited to blending vinyl chloride-grafted polymers as disclosed in Japanese Kokoku Patent No. SHO 58[1983]-56545, and conventional examples are very limited.

[0005]

Problems to be solved by the invention

In the polymer blend compositions disclosed in Japanese Kokoku Patent No. SHO 58[1983]-56545 for improving the calender molding process of polyester elastomers, the vinyl

chloride-grafted polymers blended with polyester elastomers are inferior in oil resistance and heat resistance to polyester elastomers; thus, the excellent oil resistance, thermal deformation resistance, mechanical properties, etc., of polyester elastomers are difficult to retain, and satisfactory results cannot be obtained. When calenderability improving agents (metal soaps, aliphatic amides) widely used with resins having good calenderability are used with polyester elastomers, the calenderability is not improved at all, or blooming is too severe. Also, when silicone oils disclosed in Japanese Kokai Patent No. SHO 61[1986]-195154 and inorganic hard micropowders such as talc disclosed in Japanese Kokai Patent No. SHO 58[1983]-129046 are used as sliding improving agents for polyester elastomers, or when montan ester wax disclosed in Japanese Kokai Patent No. SHO 57[1982]-8238 is used as extrusion moldability-improving agents for polyester elastomers, the calenderability is not improved at all.

[0006]

Namely, currently, the only practical technology for producing sheets and films from polyester elastomers by calendaring is the blending of polyester elastomers with vinyl chloride-grafted polymers. It is an objective of the present invention to provide calenderable polyester elastomer compositions that can be made into sheets and films retaining the characteristics of the polyester elastomer itself, with definite improvements in tackiness and adhesive properties to rolls in the calender molding process of said polyester elastomers.

[0007]

Means for solving the problems

As a result of an intense investigation for obtaining polyester elastomer sheets and films retaining the characteristics of the polyester elastomer itself and made from polyester elastomers with good calender moldability, especially with improved tackiness and adhesive properties, we have discovered that resin compositions obtained by compounding polyester elastomers with certain additives have a markedly improved calender moldability, especially with improved tackiness and adhesive properties. Thus, the present invention is attained.

[0008]

Namely, the present invention is to provide calenderable polyester elastomer compositions obtained by the melt blending of 100 parts by weight of a polyester block copolymer mainly consisting of (A) high-melting crystalline polymer segment consisting of mainly a crystalline aromatic polyester unit and (B) low-melting polymer segment consisting of mainly an aliphatic polyether unit and/or an aliphatic polyester unit, with 0.001-10 parts by weight of at least one compound selected from polyolefin wax, fluororesin powder, aromatic amine compound, and silicone resin powder.

[0009]

The high-melting crystalline polymer segment (A) of the polyester block copolymers used in the present invention is a polyester formed from (a) dicarboxylic acid or its ester-forming derivative and (b) diol or its ester-forming derivative. The dicarboxylic acids (a) may be aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,7-dicarboxylic acid, anthracenedicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, diphenoxethanedicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, 5-sulfoisophthalic acid, sodium 3-sulfoisophthalate, etc.; alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, cyclopentanedicarboxylic acid, 4,4'-dicyclohexyldicarboxylic acid, etc.; aliphatic dicarboxylic acids such as adipic acid, succinic acid, oxalic acid, sebacic acid, dodecanedioic acid, dimer acids, etc.; ester-forming derivatives of the above dicarboxylic acids, such as lower alkyl esters, aryl esters, carbonate esters, acid halides, etc. The diols (b) may be substances with molecular weights below 400, e.g., aliphatic diols such as 1,4-butanediol, ethylene glycol, trimethylene glycol, pentamethylene glycol, hexamethylene glycol, neopentyl glycol, decamethylene glycol, etc.; alicyclic diols such as 1,1-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, tricyclodecanedimethanol, etc.; aromatic diols such as xylylene glycol, bis(p-hydroxy)diphenyl, bis(p-hydroxyphenyl)propane, 2,2-bis[4-(2-hydroxyethoxy)phenyl] sulfone, bis[4-(2-hydroxy)phenyl] [sic] sulfone, 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane, 4,4'-dihydroxy-p-terphenyl, 4,4'-dihydroxy-p-quarterphenyl, etc.; ester-forming derivatives of such diols, such as acetylation products, alkali metal salts, etc.

[0010]

Two or more of such dicarboxylic acids and their ester-forming derivatives or such diols and their ester-forming derivatives may be used together. The most preferred example of segment (A) is polybutylene terephthalate derived from terephthalic acid or dimethyl terephthalate and 1,4-butanediol.

[0011]

The low-melting polymer segment (B) of the polyester block copolymers used in the present invention are aliphatic polyethers and/or aliphatic polyesters. The aliphatic polyethers may be poly(ethylene oxide) glycol, poly(propylene oxide) glycol, poly(tetramethylene oxide) glycol, poly(hexamethylene oxide) glycol, ethylene oxide-propylene oxide copolymer, poly(propylene oxide) glycol-ethylene oxide adduct polymer, ethylene oxide-tetrahydrofuran copolymer, etc. The aliphatic polyesters may be poly(ϵ -caprolactone), polycaprolactone [transliteration], polycaprylolactone, polybutylene adipate, etc. Of the aliphatic polyethers and/or aliphatic polyesters, considering the elastic properties of the resulting polyester block copolymers, preferred substances are poly(tetramethylene oxide) glycol, poly(propylene oxide) glycol-ethylene oxide adduct, poly(ϵ -caprolactone), polybutylene adipate, etc.

[0012]

The content of the low-melting polymer segment (B) of polyester block copolymers used in the present invention should be 10-90 wt%, preferably 15-75 wt%. Below 10 wt%, the softness and rubbery elasticity are not satisfactory, while above 90 wt%, the crystallinity tends to be low and the moldability is poor, thus not favored.

[0013]

The polyolefin wax used in the present invention is preferably a polyolefin wax with a molecular weight below 50,000; otherwise, there are specific restrictions. They may be obtained by the polymerization of α -olefins by a high or low-pressure process, and the molecular weight may be reduced by decomposition of the polyolefins. They may be oxidized for introduction of the carboxy group or hydroxy group into the molecule or reacted with maleic acid or epoxy-group-containing compounds, or introduced with unsaturated groups to obtain so-called modified polyolefin waxes. The α -olefins used for making polyolefin waxes may be ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene, etc. Two different α -olefins may be used together or more than two may be used together. Polyethylene waxes, polypropylene waxes, and polybutylene waxes with a molecular weight below 30,000 are preferred, while modified polyethylene waxes having a molecular weight below 10,000 and an acid value (or hydroxy value) above 10 as measured according to JIS K5902 are especially preferred. Polyethylene waxes with a molecular weight above 50,000 are not very compatible with polyester elastomers, forming molded products with a poor appearance, thus not favored.

[0014]

The fluororesin powder used in the present invention should have an average particle diameter below 100 μm , preferably below 50 μm , while there are no specific restrictions on the aggregate particle diameter, molecular weight, molecular structure, etc. Examples include polytetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-perfluorovinyl ether copolymer, and tetrafluoroethylene-ethylene copolymer pulverized to a fine powder or formed as a fine powder in polymerization. The aromatic amine compounds used in the present invention are preferably secondary or tertiary amines having the chemical structure shown below.

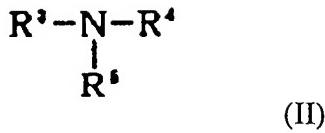
[0015]

[Chemical formula 1]



[0016]

[Chemical formula 2]



(In formula (I), at least one of R¹ and R² is an aromatic hydrocarbon moiety, with the other being an aliphatic hydrocarbon moiety. In formula (II), at least one of R³, R⁴, and R⁵ is an aromatic hydrocarbon moiety, with the other being an aliphatic hydrocarbon moiety.) Examples of the compounds represented by formula (I) and (II) include ethylaniline, diethylaniline, triphenylamine, α-naphthylamine, β-naphthylamine, phenyl-α-naphthylamine, phenyl-β-naphthylamine, p,p'-dioctyldiphenylamine, N,N'-diphenyl-p-phenylenediamine, 4,4'-bis(4-α,α-dimethylbenzyl)diphenylamine, 4,4'-bis(α-methylbenzyl)diphenylamine, 4,4'-bis(α-methyl-α-ethylbenzyl)diphenylamine, 4-(α-methylbenzyl)-4'-(α-ethylbenzyl)diphenylamine, etc.

[0017]

The silicone resin powder used in the present invention should have an average particle diameter below 100 μm, preferably below 50 μm, while there are no specific restrictions on the aggregate particle diameter, molecular weight, molecular structure, mechanical properties, etc., e.g., mainly a dimethylpolysiloxane-based tridimensionally crosslinked resin pulverized to a fine powder or formed as a fine powder in polymerization.

[0018]

The content of compounds used in the present invention should be 0.001-10 parts by weight, preferably 0.01-5 parts by weight, to 100 parts by weight of the polyester elastomer. Below 0.001 part by weight, improvement in roll sticking and adhering properties is not sufficient, while above 10 parts by weight, the polyester elastomer's mechanical properties tend to be inferior.

[0019]

There are no specific restrictions on ways to add such compounds to polyester block copolymers; they can be added to polyester block copolymers in the molten state immediately after being prepared; added to polyester block copolymer chips, followed by melt mixing; added to polyester block copolymer chips by dry blending immediately before calendaring for inclusion in the calender molding process; or added to a molten or semi-molten polyester block copolymer sheet during calendaring. The temperature upon melt addition to the polyester block copolymer should be in the range from 10°C below the polyester block copolymer's melting point to 280°C. The mixing time should be from several seconds to 120 min, depending on the mixing temperature and mixing method.

[0020]

Within the range having no adverse effects on the objectives of the present invention, the compositions of the present invention may also contain a known hindered phenol, benzophenone, phosphite, and hindered amine-type antioxidants; benzophenone, hindered amine-type weather stabilizers, thickeners such as epoxy compounds, isocyanate compounds, etc.; mold release agents such as silicone oil, stearic acid metal salts, montan acid metal salts, montan ester waxes, etc.; colorants such as dyes, pigments, etc.; UV shields such as titanium oxide, carbon black, etc.; reinforcements such as glass fibers, carbon fibers, potassium titanate fibers, etc.; fillers such as silica, clays, calcium carbonate, calcium sulfate, glass beads, etc.; nucleating agents such as talc, etc.; fire retardants; plasticizers; foaming agents; fluorescent whiteners; fungicides; crosslinking agents; surfactants, etc.

[0021]

Such fillers and additives may be compounded with polyester block copolymers first or compounded with the compositions of the present invention together with polyester block copolymers, or compounded after molding of the compositions of the present invention.

[0022]

Function

In the calender molding process with the compositions of the present invention, prevention of tackiness and adhesion to the roll is good, and moldings have an excellent surface appearance and mechanical properties.

[0023]

Examples

Next, effects of the present invention are explained with examples. In the examples, % and parts are by weight. The physical properties given in the examples are measured as shown below.

Melting point: Measured by DSC method.

[0024]

Hardness (Shore D scale): Measured according to ASTM K-7215.

Melt viscosity index (MFR value): Measured according to ASTM D-1238 at 200°C under a 2160-g load.

Calender molding test: Using two 8-inch rolls of the Nippon Roll Co., polyester block copolymer pellets are dry blended with the desired calenderability improving agents; in some cases, raw material that had been melt blended and pelletized is fed between the rolls and measured for the time needed to stick to the rolls (roll lubricity retention time).

[0025]

Alternatively, after 20 min, peelability from the rolls is evaluated in 5 grades. A peelability of 5 is given for total peeling without any resistance, comparable to the case of

ordinary vinyl chloride; 4 is somewhat inferior to 5; 3 indicates difficulty in mass production; 2 is for poor peeling, considered to be a difficulty in calendering; and 1 is for no peeling at all.

Molding appearance: Visual evaluation of the surface of a 500- μm -thick calender sheet.
[0026]

Tensile strength and elongation: Measured at a strain level of 400% using a JIS No. 2, 45% punch piece from a 500- μm -thick calender sheet.

Oil resistance: The above tensile test sample is immersed in JIS No. 3 oil at 120°C for 300 h, then the elongation retention is measured.

Reference Example

Polymerization of polyester elastomer (A-1)

In a reactor fitted with a helical ribbon stirring blade, 194 parts of dimethyl terephthalate, 265.4 parts of poly(tetramethylene oxide) glycol with a number-average molecular weight of about 1000, 69.6 parts of tetramethylene glycol, and 0.10 part of titanium tetrabutoxide were heated at 190-225°C for 2 h with distillation of 95% of the theoretical amount of methanol, treated with 0.5 part of Irganox 1010 (hindered-phenol-type heat stabilizer, product of CIBA-GEIGY Co.), heated to 245°C, with the interior pressure being reduced to 0.2 mm Hg over a period of 50 min, and the polymerization is continued under the same conditions for 2 h. The polymer formed was extruded in a strand into water and cut into pellets to obtain polymer A-1.

[0027]

Polymerization of polyester elastomer (A-2)

In a reactor fitted with a helical ribbon stirring blade, 155.2 parts of dimethyl terephthalate, 38.8 parts of dimethyl isophthalate, 290 parts of ethylene oxide-capped poly(propylene oxide) glycol (number-average molecular weight: about 2200, EO content: 26.8%), 82.2 parts of tetramethylene glycol, 0.10 part of titanium tetrabutoxide, and 2 parts of trimellitic anhydride were heated at 210°C for 2 h with distillation of 95% of the theoretical amount of methanol, treated with 0.5 part of Irganox 1010, heated to 245°C, with the interior pressure being reduced to 0.2 mm Hg over a period of 50 min, and the polymerization was continued under the same conditions for 2 h. The polymer formed was extruded in a strand into water and cut into pellets to obtain polymer A-2.

[0028]

Polymerization of polyester elastomer (A-3)

In a reactor fitted with a helical ribbon stirring blade and a distillation tower, 100 parts of terephthalic acid, 110 parts of 1,4-butanediol, and 0.10 part of titanium tetrabutoxide were stirred with the distillation of water formed by the reaction for esterification in a nitrogen atmosphere under ambient pressure for 2 h. The reaction product was transferred into a polymerization can

and heated at 250°C and 0.2 mm Hg for 2 h for polymerization. The polymer formed was extruded in a strand into water and cut into pellets to obtain polybutylene terephthalate having a relative viscosity of 1.47 and melting point of 225°C. This polybutylene terephthalate and ε-caprolactone were fed at 900 g/h and 1700 g/h, respectively, into a feed opening at the back end of a single-screw extruder having a 200-mm-long kneading unit in the middle and front parts, internal diameter of 30 mm φ, and L/D = 40, cylinder middle-part temperature of 240°C, and screw rotation of 30 rpm. The polymer formed was extruded through a die in a strand form and cut to obtain pellets. In a vented single full-flight screw extruder with an internal diameter of 30 mm φ and L/D = 40, 100 parts of the pellets and 0.1 part of triphenyl phosphite were kneaded under a vent vacuum of 10 mm Hg, extrusion temperature of 200°C, and screw rotation of 60 rpm for ε-caprolactone removal and catalyst deactivation. The polymer was extruded in a strand form through a die and cut to pellets to obtain polymer A-3.

[0029]

Compositions and properties of A-1, A-2, and A-3 are given in Table 1.

Table 1

	Copolymerized amount of poly(tetramethylene oxide) glycol (wt%)	Copolymerized amount of poly(propylene oxide) glycol (wt%)	Copolymerized amount of polycaprolactone (wt%)	Melting point (°C)	Shore D hardness	Melt viscosity index (g/10 min)
A-1	65			165	38	8
A-2		62		155	34	13
A-3			65	171	39	26

Application Examples 1-9

The polyester elastomer A-1 obtained in the Reference Example was dry blended with polyolefin waxes (B-1-1) ~ (B-1-3), fluororesin powders (B-2-1) and (B-2-2), aromatic amine compounds (B-3-1) and (B-3-2), and silicone resin powders (B-4-1) and (B-4-2) shown in Table 2, in proportions shown in Table 3, and subjected to a calender molding test at a roll temperature of 165°C. The compounds used are given in Table 2. Evaluation results of Application Examples 1-9 are given in Table 3.

Comparative Examples 1-7

Polymer A-1 of the Reference Example and polymer A-1 dry blended with known compounds (C-1) ~ (C-6) shown in Table 2, in ratios given in Table 3, were evaluated similarly as in Application Example 1.

[0030]

Also, (E) (vinyl chloride resin) of Table 2 dry blended with 1% of (C-2) was tested at a roll temperature of 160°C. Evaluation results of Comparative Examples 1-7 are given in Table 3.

[0031]

Table 2

Additives	Additive names	Additive manufacturers, Tradenames	Others
B-1-1	Polyethylene wax	Mitsui Petrochemicals, 110P	Unmodified molecular weight: 1,000
B-1-2	"	Mitsui Petrochemicals, 2203A	Modified Acid value: 30 KOH mg/g Molecular weight: 2,700
B-1-3	Polypropylene wax	Sanyo Kasei Kogyo, Youmex 1201	Modified Hydroxy group value: 31 KOH mg/g Molecular weight: 15,000
B-2-1	Fluororesin powder	Mitsui Dupont Fluorochemical, Teflon K-10	Average particle diameter: 0.2 μm
B-2-2	"	Mitsui Dupont Fluorochemical, Teflon MP-1500J	Average particle diameter: 20 μm
B-3-1	Aromatic amine	Uniroyal, Naugard 445	4,4'-bis(4-α,α-dimethyl benzyl) diphenylamine
B-3-2	"	Uniroyal, Naugard PANA	Phenyl-α-naphthylamine
B-4-1	Silicone resin powder	Toray-Dow Corning Silicone, Trefil R900	Average particle diameter: 20 μm
B-4-2	"	Toray-Dow Corning Silicone, Trefil E500	Average particle diameter: 3 μm
C-1	EVA-PVC graft polymer	Nippon Zeon, Graftmer R-5	EVA/PVC weight ratio: 1/1
C-2	Zinc stearate		
C-3	Ethylenebisstearylamine	Daiichi Kogyo, EBA	
C-4	Silicone oil	Toray-Dow Corning Silicone, SH 200	
C-5	Talc	Takehara Kagaku Kogyo, High Toron	
C-6	Montanester wax	Hoechst, Hoechst Wax OP	
E	PVC (vinyl chloride resin)		Containing 40 wt% of DOP

[Some tradenames are transliterations.]

[0032]

Table 3

Examples	Polymers	Additives					Added amount, parts by weight	Roll lubricity retention time (min)	Sheet peeling	Sheet surface appearance	Tensile properties Strength (kg/cm ²)	Elongation (%)	Oil resistance Elongation retention (%)
		B-1	B-2	B-3	B-4	C							
Application Example 1	A-1	B-1-1					0.6	25	4	Good	250	1200	82
Application Example 2	A-1	B-1-2					0.5	50	5	Good	280	1100	88
Application Example 3	A-1	B-1-3					0.5	30	4	Good	274	1090	95
Application Example 4	A-1		B-2-1				0.5	40	5	Good	307	1050	92
Application Example 5	A-1		B-2-2				0.5	33	5	Good	314	1070	86
Application Example 6	A-1			B-3-1			0.6	> 60	4	Good	299	1180	80
Application Example 7	A-1			B-3-2			0.6	40	4	Good	280	1200	98
Application Example 8	A-1				B-4-1		0.6	25	4	Slightly poor	323	980	83
Application Example 9	A-1				B-4-2		0.6	37	4	Good	287	1150	105
Comparative Example 1	A-1	-	-	-	-	-	-	< 1					
Comparative Example 2	A-1					C-1	0.5	2					
Comparative Example 3	A-1					C-2	0.5	2					
Comparative Example 4	A-1					C-3	0.5	< 1					
Comparative Example 5	A-1					C-4	0.5	< 1					
Comparative Example 6	A-1					C-5	0.5	< 1					
Comparative Example 7	E					C-2	1.0	48	5	Good	80	460	< 10

Application Examples 10-13

The polyester elastomer A-1 obtained in the Reference Example was first mixed with 3.0 parts by weight of (B-1-2), (B-2-1), (B-3-1), and (B-4-1) among the additives used in Application Examples 1-9 using a V-blender, melt-kneaded and pelletized using a biaxial extruder of 45 mm φ at 190°C, and evaluated similarly as in the Reference Example.

[0033]

Evaluation results of Application Examples 10-13 are shown in Table 4.

Comparative Example 8 and 9

Polymer A-1 of the Reference Example and polymer A-1 containing known additives (C-1)~(C-5) shown in Table 2 were evaluated similarly as in Application Examples 10-13. Evaluation results are shown in Table 4.

[0034]

Table 4

Examples	Polymers	Additives					Added amount, parts by weight	Roll lubricity retention time (min)	Sheet peeling	Sheet surface appearance	Tensile properties Strength (kg/cm²) Elongation (%)	Oil resistance Elongation retention (%)
		B-1	B-2	B-3	B-4	C						
Application Example 10	A-1	B-1-2					3.0	78	5	Good	250 810	81
Application Example 11	A-1		B-2-1				5.0	80	5	Good	310 1010	93
Application Example 12	A-1			B-3-1			5.0	>60	4	Some discoloration	300 960	85
Application Example 13	A-1				B-4-1		5.0	>60	5	Good	230 750	96
Comparative Example 8	A-1					C-1	10.0	28	5	Good	280 850	53
Comparative Example 9	A-1					C-2	30.0	51	5	Good	260 700	37

Application Examples 14-18

The polyester elastomer A-1 obtained in the Reference Example was compounded with two or more different compounds shown in Table 2 in the combinations shown in Table 5, then evaluated similarly as in Application Examples 1-9.

[0035]

The evaluation results of Application Examples 14-18 are shown in Table 5.

Comparative Examples 9 and 10

The polymer A-1 of the Reference Example compounded with known compounds (C-1) and (C-2), as well as (C-1) and (C-3) shown in Table 2, were evaluated similarly as in Application Examples 14-18. The evaluation results are given in Table 5.

[0036]

Table 5

Examples	Polymers	Additives					Added amount, parts by weight	Roll lubricity retention time (min)	Sheet peeling	Sheet surface appearance	Tensile properties Strength (kg/cm²) Elongation (%)	Oil resistance Elongation retention (%)
		B-1	B-2	B-3	B-4	C						
Application Example 14	A-1	B-1-1	B-2-1				0.5 0.1	>60	5	Good	260 1060	86
Application Example 15	A-1	B-1-2		B-3-1			0.5 0.05	62	5	Good	300 1020	99
Application Example 16	A-1			B-3-1	B-4-1		0.5 0.1	55	5	Good	230 990	98
Application Example 17	A-1	B-1-2	B-2-1	B-3-1			0.5 0.1 0.1	>70	5	Good	305 1040	88
Application Example 18	A-1	B-1-2	B-2-1	B-3-1	B-4-1		0.5 0.01 0.05 0.01	>70	5	Good	290 1100	100
Comparative Example 9	A-1					C-1 C-2	10.0 0.5	37	5	Good	290 920	62
Comparative Example 10	A-1					C-1 C-3	10.0 0.5	30	5	Good	270 1010	65

Application Examples 19-26

Experiments were carried out similarly as in Application Examples 1-9 using polyester elastomers A-2 and A-3 in place of polyester elastomer A-1 of the Reference Example, then evaluated.

[0037]

In the calender molding test, the roll temperature was 152°C with A-2 and 170°C with A-3. Results are given in Table 6.

Comparative Examples 11 and 12

Polymers A-2 and A-3 of the Reference Example were evaluated similarly as in Application Examples 19-26.

[0038]

Evaluation results are given in Table 6.

Table 6

Examples	Polymers	Additives					Added amount, parts by weight	Roll lubricity retention time (min)	Sheet peeling	Sheet surface appearance	Tensile properties Strength (kg/cm ²)	Elongation (%)	Oil resistance Elongation retention (%)
		B-1	B-2	B-3	B-4	C							
Application Example 19	A-2	B-1-2					0.5	55	4	Good	330 700		100
Application Example 20	A-2		B-2-1				0.5	46	5	Good	340 710		85
Application Example 21	A-2			B-3-1			0.5	60	5	Good	330 705		90
Application Example 22	A-2				B-4-1		0.5	41	4	Good	305 680		98
Application Example 23	A-2	B-1-2		B-3-1			0.5 0.1	>60	5	Good	345 740		88
Application Example 24	A-2	B-1-2	B-2-1	B-3-1			0.5 0.1 0.1	>60	5	Good	330 730		97
Application Example 25	A-3	B-1-2					0.5	40	5	Good	295 1050		85
Application Example 26	A-3	B-1-2	B-2-1	B-3-1			0.5 0.1 0.1	54	5	Good	300 1020		88
Comparative Example 11	A-2	-	-	-	-	-	-	<1					
Comparative Example 12	A-3	-	-	-	-	-	-	<1					

Results in Table 3 show that with the addition of a small amount of additives, the compositions of the present invention exhibit a significantly improved calender molding processability, with especially improved roll sticking and adhesion properties, while an excellent balance of mechanical properties and surface appearance is maintained. Furthermore, as shown by the results in Table 4, similar results can be obtained with increased amounts of the compounds added.

[0039]

As shown in Table 5, similar results can be obtained by adding two or more different compounds. Good roll sticking prevention can also be obtained by blending such compounds with A-2 or A-3 having a soft segment different from the polyester elastomer A-1 as shown in Table 6, indicating that roll sticking prevention of polyester elastomers can be greatly improved regardless of the type of soft segments of polyester elastomers.

[0040]

Effects of the invention

According to the present invention, polyester block copolymers melt-mixed with certain compounds exhibit a calenderability comparable to vinyl chloride and EVA. In particular, roll sticking and adhesion can be greatly reduced, forming polyester elastomer sheets and films with an excellent surface appearance and mechanical properties.